



The effect gas composition during thermal aging on the dispersion and NO oxidation activity over Pt/Al₂O₃ catalysts

Xavier Auvray^a, Torben Pingel^b, Eva Olsson^b, Louise Olsson^{a,*}

^a Competence Center for Catalysis, Chemical Engineering, Chalmers University of Technology, S-412 96 Göteborg, Sweden

^b Competence Center for Catalysis, Department of Applied Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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ABSTRACT

The aging of a model 1 wt.% Pt/Al₂O₃ catalyst was performed stepwise under different reactive atmosphere to study the evolution of metal dispersion and NO oxidation activity. After each aging step the dispersion was evaluated by CO chemisorptions and the activity of the catalyst for NO oxidation was measured using 500 ppm NO and 8% O₂ diluted in Ar. After a degreening step at 500 °C, aging was performed at 600, 700, 800 and 900 °C. Five wash-coated cordierite monoliths were aged in Ar, 10% O₂, 1% H₂, 30 ppm SO₂ and 30 ppm SO₂ + 10% O₂, respectively. The general trend showed a linear decrease in dispersion when increasing the aging temperature for the lower aging temperatures and for the highest ones the dispersion levels off. When the platinum dispersion decreased the NO oxidation activity increased, due to that the reaction is structure sensitive. H₂ seemed to hinder sintering at low aging temperature. Interestingly, after aging in 10% oxygen at 600 °C the NO oxidation activity was significantly higher compared to the Ar aged sample, although the dispersions were similar. Aging in oxygen at higher temperatures resulted in a decrease of dispersion and a slightly decreasing NO oxidation activity. Moreover lower dispersion limit was reached with oxygen aging. Aging in SO₂ provoked a severe dispersion drop at low aging temperature meanwhile the activity increased only moderately. However, activity kept increasing with further treatments at higher temperature. The combination of O₂ and SO₂ enabled to decrease rapidly the dispersion and to greatly enhance the catalytic NO oxidation activity after the first aging step at only 600 °C. The best overall conversion was obtained for the catalyst treated with this mixture after aging at 800 °C. A 22-h aging at 250 °C in a mixture containing 500 ppm NO, 10% O₂ and 30 ppm SO₂ led to a significant decrease of Pt dispersion, which shows the ability of SO₂ to promote platinum sintering already 250 °C. The low temperature sintering was confirmed with STEM measurements. Several larger particles were observed, but also many small particles remained. Thus the SO₂ + O₂ induced low temperature sintering results in a large variation of particle sizes. This treatment resulted in an increase of the maximum NO conversion (after reduction of the sample) from 45% to 76%. The different aging experiments show that it is beneficial to add SO₂ during aging and the reason is the increased particle size, but also a clear chemical effect was observed.

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1. Introduction

For economical and environmental reasons, the consumption of fossil fuel needs to be reduced. It is therefore beneficial to use vehicles equipped with diesel or lean-burn gasoline engines that have a better fuel economy. In these types of engines the combustion is done with an excess of air. However, the standard three-way catalyst (TWC) cannot reduce the formed NO_x species (i.e. NO and NO₂) with high efficiency. NO_x are harmful compounds responsible for acid rain, it reacts with hydrocarbons to produce ground level

ozone, which is major component of smog and NO_x also increases the risk for respiratory allergies. It is therefore crucial to remove these compounds by the exhaust gas after-treatment of the vehicle. There are two techniques that have been developed to reduce NO_x in these conditions. The NO_x storage reduction (NSR) implies the oxidation of NO and the subsequent storage as nitrates species on the catalyst. During cyclic short periods the engine works in fuel-rich condition to release and reduce the stored species into N₂ and water. The second method involves injecting an additional reductant that can selectively and continuously reduce the NO_x, the so called selective catalytic reduction process (SCR). A common reductant is urea, which decomposes and hydrolyses to form NH₃. The NH₃ SCR process is optimized when a mixture containing NO and NO₂ in equal proportions is used. An oxidation of NO

* Corresponding author. Tel.: +46 31 772 4390; fax: +46 31 772 3035.

E-mail address: louise.olsson@chalmers.se (L. Olsson).

prior to the SCR catalyst is therefore valuable. In addition, the NO_2 is also beneficial for regeneration of diesel particulate filters (DPF).

NO oxidation is a key reaction for NO_x removal and has been individually studied over Pt-based catalysts [1–5]. At low temperature the reaction is limited by the kinetic rates, while the thermodynamic equilibrium is the limiting factor at high temperature. The activity of the catalyst increases with Pt loading [5] as well as O_2 partial pressure [6] up to 10% but the concentration of NO tends to lower the conversion [6]. The impact of different supports on the Pt-based catalysts performance has also been compared and the catalytic activity follows the order: $\text{Pt}/\text{SiO}_2 > \text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{ZrO}_2$ [1,5].

Thermal aging occurs during the lifetime of an automotive catalyst and that leads to a change in catalytic behavior. At elevated temperature platinum crystallites sinter and, as a result, the dispersion of the catalyst drops and the mean particle size increases. In many studies it is observed that large Pt particles are more active than small particles for NO oxidation, despite the less number of available sites [1,4,5,7–9]. Thus a thermal aging can enhance the performance of the catalyst. The temperature, the duration of treatment and the atmosphere of the aging step are parameters that influence the rate of sintering. Chu and Ruckenstein [10] showed that the sintering of Pt crystallites was not significant when the catalyst was aged in vacuum, O_2 , H_2 and N_2 even at 750°C but important sintering occurs already at 500°C in humid H_2 . Stenbom and Löff [11,12] noticed a significant sintering of $\text{Pt}/\text{Al}_2\text{O}_3$ due to O_2 treatment at 600 and 700°C and found a strong effect of NO on particle growth. Lee and Kim [13] revealed the redispersing effect on $\text{Pt}/\text{Al}_2\text{O}_3$ using O_2 below 600°C and the opposite impact at higher temperature causing severe sintering in agreement with the model proposed by Flynn and Wanke [14]. This result could explain the differences in results for the effect of O_2 . SO_2 has an interesting beneficial effect on the platinum sintering [16]. Karlsson and Olsson [16] observed that sintering of platinum on $\text{Pt}/\text{Al}_2\text{O}_3$ occurred already at 200°C , when exposing the catalyst to SO_2 , NO and O_2 for 22 h. Aging atmosphere has various consequences on the platinum particles [17] and different aging treatments lead to particles with different size and properties, which is a crucial factor to the oxidation of NO . However, the activity of $\text{Pt}/\text{Al}_2\text{O}_3$ towards the oxidation of NO after various aging treatment has not been investigated yet to the best of our knowledge. In addition, there is very limited research done on the influence of SO_2 on the sintering.

In this work, we investigate the NO oxidation activity and platinum dispersion of a model $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst after several aging steps at temperature ranging from 600 to 900°C and in different gas mixtures. The atmospheres investigated were Ar, 10% O_2 , 1% H_2 , 30 ppm SO_2 and 30 ppm SO_2 + 10% O_2 with Ar as carrier gas.

2. Experimental

2.1. Catalyst preparation

The $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst powder was prepared by wet impregnation of a solution of alumina (Puralox SBA-200 Sasol) previously calcined for 2.5 h at 750°C in air in order to prevent morphological changes after metal deposition. The pH of alumina slurry was maintained at 4 by adding diluted solution of HNO_3 or NH_3 . The slurry was kept under constant stirring. The Pt-containing solution was prepared by dilution of $\text{Pt}(\text{NO}_3)_2$ (Heraeus GmbH 15.46 wt.%) in milliQ water. The aqueous solution of Pt was added dropwise to the alumina slurry and stirred for 1 h. The pH was then checked and adjusted, if needed, to $\text{pH}=2$. The solution was freeze-dried and the resulting $\text{Pt}/\text{Al}_2\text{O}_3$ powder was calcined for 2 h at 500°C in

air to remove impurities left by the precursor like nitrates ions. The powder had a Pt loading of 1 wt.%.

The samples were prepared by deposition of the catalyst powder described above onto monoliths. The monoliths ($\varnothing=20$ mm, length = 22 mm) were extracted from a commercial honeycomb cordierite structure with a channel density of 400 cpsi. A mixture of powder containing 80 wt.% of the catalyst and 20 wt.% of a binder (Disperal sol Condea) was diluted in an ethanol solution (water 1:1 ethanol). The monoliths were dipped into the obtained slurry under vigorous stirring. After that an homogeneous covering of the monolith walls by the solution was obtained, the excess of solution was removed and the deposited layer was dried and calcined with an air gun at 600°C for 1 min. The dipping and drying operation was repeated until the correct amount of washcoat (≈ 20 wt.%) was deposited onto the internal walls of the monolith. The monoliths obtained were calcined in air at 500°C for 2 h. Details from the different monoliths can be found in Tables 1 and 2.

2.2. Specific surface area

The specific BET surface area of the monoliths was measured by physisorption of N_2 at 77K using a Micromeritics ASAP2010 instrument. The samples were first evacuated at 225°C for 2 h. The results are reported in Table 2.

2.3. Transmission electron microscopy

Transmission electron microscopy (TEM) studies were performed to compare platinum particle sizes before and after different treatments. After aging, catalyst powder was collected from the monolith for TEM analysis. The catalysts were pestled in an agate mortar and the resulting powder was subsequently put on holey carbon films on TEM Cu grids. The particles were imaged using an FEI Titan 80–300 TEM with a probe Cs (spherical aberration) corrector operated at 300 kV. The images were recorded using a high angle annular dark field (HAADF) detector in the scanning TEM imaging mode (STEM), providing Z number contrast. The electron probe size was about 0.2 nm for these studies.

2.4. Reactor setup

The activity test, the aging treatment and the dispersion measurement were performed in a bench reactor. The monolithic sample was wrapped with quartz wool to limit gas bypassing and placed in an inert quartz tube. The composition of the gas flow was controlled by a gas mixer (Enviroics 2000). The temperature was measured by three K-type thermocouples inserted in the reactor from the outlet. The thermocouple controlling the inlet temperature was placed 2 cm upstream of the catalyst and was connected to a Eurotherm temperature controller in order to regulate the heating. A second thermocouple was inserted in the center channel of the sample and the third one measured the temperature of the gas exiting the catalyst. About 1 cm downstream an empty cordierite monolith was placed in order to decrease the temperature gradient over the sample, by reducing the heat losses due to radiation. Through experiments we ensured that the cordierite did not store NO and NO_2 nor disturb the measurements.

The heating was provided by a resistive coil surrounding the tube controlled by the Eurotherm temperature controller. The reactor was wrapped in a thick layer of insulating wool to insure good temperature homogeneity.

To analyze the composition of the outlet gas, the reactor was equipped with a chemiluminescence-based NO_x analyzer (ECO physics CLD 700 EL ht) and two infra-red detectors (Maihak

Table 1

Results of dispersion and NO conversion for all the samples and all aging steps.

Aging status	Degreened (500 °C)	600 °C	700 °C	800 °C	900 °C
M-Ar					
Dispersion (%)	62	43	23	18	18
Max conversion (%)	40	49	57	61	68
T max conversion (°C)	400–410	375–400	350–370	350–360	325–340
M-H ₂					
Dispersion (%)	75	71	52	24	16
Max conversion (%)	46	48	60	68	78
T max conversion (°C)	385–395	380–390	340–360	325–345	290–310
M-O ₂					
Dispersion (%)	80	52	30	8	7
Max conversion (%)	48	71	75	73	69
T max conversion (°C)	380	325–335	310–320	305–330	310–330
M-SO ₂					
Dispersion (%)	91	20	10	27	21
Max conversion (%)	39	47	65	80	86
T max conversion (°C)	405–420	385–390	330–350	290–310	260–280
M-SO ₂ /O ₂					
Dispersion (%)	77	14	4	4	4
Max conversion (%)	45	76	78	88	81
T max conversion (°C)	390	290–310	270–310	245–270	260–280

UNOR 6N) monitoring the concentrations of CO and CO₂ respectively.

2.5. Dispersion measurement by CO chemisorption

CO adsorption on Pt was performed at 25 °C in the reactor. The catalyst was first heated to 400 °C, where it was exposed for 40 min to a flow of 1 L/min containing 2% H₂, with Ar as inert balance. For the sample which was aged at low temperature in the presence of sulphur, for 22 h (described in a later section) the reduction occurred at 450 °C in 2% H₂ for 30 min. The reason for the higher reduction temperature was that the sample likely adsorbed large amounts of sulfur during 22 h at 250 °C. After rapid cooling in the same reducing stream, pure Ar flowed through the catalyst for 10 min in order to remove traces of H₂. The CO adsorption was carried out in two pulses composed of 100 ppm CO (1 L/min) during 20 min and 10 min, respectively. Under the first pulse, CO adsorbed on Pt. The catalyst was then flushed for 7 min with an Ar flow to remove weakly bonded CO molecules. Under the second exposure, only weakly bonded CO was adsorbed. The outlet concentration was monitored and CO uptake of each pulse could be found by integration. The first adsorption represents the total uptake of CO and the adsorption quantified in the second pulse corresponds to the physisorbed CO and the response of the empty reactor. Thus the subtraction of the weakly bonded CO from the first uptake yields adsorption of chemisorbed CO. The number of platinum atoms on the surface (Pt_{surf}) is correlated to the amount of CO chemisorbed. On platinum, CO can bind both linearly and bridged. We have used a

factor of 0.8 CO/Pt according to Fogar and Anderson [18] and Olsson et al. [19].

2.6. Catalytic activity – NO oxidation

After CO chemisorption experiment, the NO oxidation activity was measured in dry conditions by flowing a mixture of 8% O₂, 500 ppm NO in Ar (total flow 3 L/min) through the catalyst. After a 5 min purge with pure Ar, the reaction mixture was sent over the catalyst for 25 min at ambient temperature to saturate the surface. We observed that the initial concentration of 500 ppm NO was recovered at the outlet after about 15 min.

Then the temperature was linearly increased at a rate of 5 °C/min up to 500 °C. This temperature was held for a short time (4 min) in order to get a stable final temperature.

2.7. Pretreatment and aging of the catalysts

The fresh samples, prepared from the same catalyst powder batch, were degreened at 500 °C for 2 h in a flow containing 8% O₂ and 500 ppm NO in Ar (3 L/min).

Each sample was aged at 600, 700, 800 and 900 °C in various atmosphere (Ar, 1% H₂/Ar, 10% O₂/Ar, 30 ppm SO₂/Ar and (30 ppm SO₂ + 10% O₂)/Ar). Aging was performed in dry conditions. The sample was rapidly heated up to the aging temperature in a flow of 1 L/min of Ar. Then the gas composition was switched to the aging atmosphere specific to each sample; the total flow remained unchanged. The temperature was maintained for 2 h and after that the cooling started when exposing the catalyst to Ar only.

An aging atmosphere was attributed to each sample which was then aged successively at 600, 700, 800 and 900 °C. After the degreening and after each aging the dispersion and the activity of the catalyst were evaluated as described above. It should be pointed out that after the aging the CO chemisorption, which included hydrogen pretreatment, was conducted first. After this NO oxidation was performed. Thus, the platinum was reduced with hydrogen after the aging before measuring dispersion and activity.

A different aging treatment was performed on a sixth sample prepared as previously described from the same catalyst batch. The catalyst was aged in a flow composed of 500 ppm NO, 8% O₂ and 30 ppm SO₂ at 250 °C for 22 h to investigate the effect of a long-term

Table 2

Results from BET measurements of fresh and catalysts aged at 900 °C.

Sample	BET surface area FRESH		BET surface area AGED	
	m ² /g _{monolith}	m ² /g _{washcoat}	m ² /g _{monolith}	m ² /g _{washcoat}
M-SO ₂ /O ₂	43.9	174.6	35.9	146.7
M-O ₂	35.5	176.9	30.7	155.3
M-Ar	30.9	162.3	25.9	139.2
M-SO ₂	20.1	167.7	18.4	155.9
M-H ₂	20.8	148.3	19.9	144.4
M-long aging	20.9	162.1	20.6	161.8

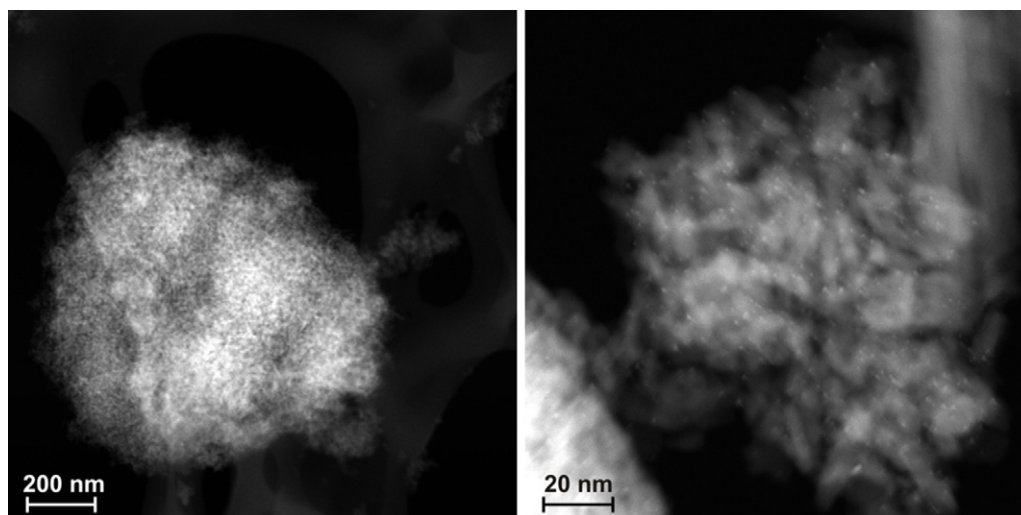


Fig. 1. STEM images of the fresh Pt/Al₂O₃ catalyst.

exposure to SO₂ at low temperature. The total flow was 3 L/min and Ar was the carrier gas.

3. Results

3.1. Characterization of the fresh catalysts

The dispersion of the catalysts was measured and is displayed in Table 1. The degreened samples showed an high initial dispersion. In addition, Scanning TEM (STEM) images of the fresh catalyst powder (after hydrogen reduction) were taken and are shown in Fig. 1. No large particles were detected, as seen on the left-side image. The right-side image (Fig. 1), which was taken using higher magnification, reveals several small platinum particles (about 1 nm), homogeneously spread over the catalyst particle. The STEM results are in good agreement with the assessed dispersion. In addition, the BET surface area was measured and the results are shown in Table 2. The loss of surface area is mainly due to high temperature treatment since no significant decrease was measured on the sample treated at 250 °C unlike the samples aged at high temperature. Interestingly the sample aged in H₂ kept a surface area close to its initial value.

3.2. Pt Sintering and NO oxidation activity

The sintering of the platinum particles was examined by measuring the metal dispersion after each aging step. Fig. 2a shows the platinum dispersion for the monolith aged in pure argon (M-Ar) versus the temperature of aging. The values of temperature reported in abscissa are the intra-catalyst temperature during the 2-h aging step and differ slightly from the inlet gas temperature. It should be mentioned that during the preparation of the monoliths the catalysts were calcined in hot air flow for 1 min at 600 °C after each addition of wash-coat, which was followed by calcination for 2 h in air at 500 °C. Since Ar is an inert gas, temperature is the only sintering factor for M-Ar. In Fig. 2a the dispersion of Pt decreased linearly until the treatment at 700 °C and then it leveled off. It seems that the dispersion has reached a limit of about 18%. At low dispersion, the particles are far from each other and further sintering requires a high mobility over long distances. In that context, a 2-h aging, even at high temperature, may be too short to have a noticeable impact. This could be the reason for the same dispersion after 800 and 900 °C aging.

The conversion of NO is calculated from the measured concentrations of NO and NO₂, which is shown for the different aging temperatures in Fig. 2b. The NO oxidation experiment was always performed after the dispersion measurement, which included pre-treatment with hydrogen. The NO₂ concentration is increasing with increasing temperature for the low temperature region and decreases for higher temperatures. The reason is that the reaction is limited by the kinetics at low temperature and by the thermodynamics at high temperature. The performance of the catalyst was progressively enhanced after each aging. These results are in line with earlier studies [1,2,6,20]. The maximum conversion became higher and the reaction started to occur at lower temperature, broadening the operating window of the catalyst. The maximum conversion appears in a temperature window ranging from 300 to 400 °C depending on the aging state of the catalyst. However a shoulder appeared at low temperature (ca. 240 °C) for mild-aged catalyst.

The oxidation of NO to NO₂ has been described as a structure sensitive reaction [3–5,8] which means that the size and the structure of the particles have an influence on the activity. In our case, larger Pt particles exhibited better activity than smaller particles. From the results in Fig. 2b the maximum NO conversion reached during the experiments can be observed. These values are shown versus aging temperature in Fig. 2c. While the dispersion decreased rapidly up to 700 °C and thereafter decreased with a lower rate (see Fig. 2a), the activity kept increasing linearly. Interestingly, the activity increase did not show the same trend as the decrease in dispersion during aging. Thus, the platinum dispersion is likely not the only factor that determines the NO oxidation activity. For example, the activity was increased significantly by the last aging at 900 °C (see Fig. 2b and c), while the dispersion remained constant at 18%. This discrepancy reveals that particles have properties influencing the catalytic performance other than the dispersion.

3.3. Effect of H₂

A second Pt/Al₂O₃ catalyst, denoted M-H₂ (see Table 1), was aged in 1% H₂. The effect of progressive aging on Pt dispersion and activity are shown in Fig. 3, together with the results for the sample aged in Ar only (M-Ar). There is a difference in the initial dispersion of the two samples. However, a clear trend is observed that the sample aged in the presence of H₂ has a lower sintering rate at lower temperature. The final dispersion after 800 and 900 °C aging of M-H₂ is comparable to the one of M-Ar. Despite their

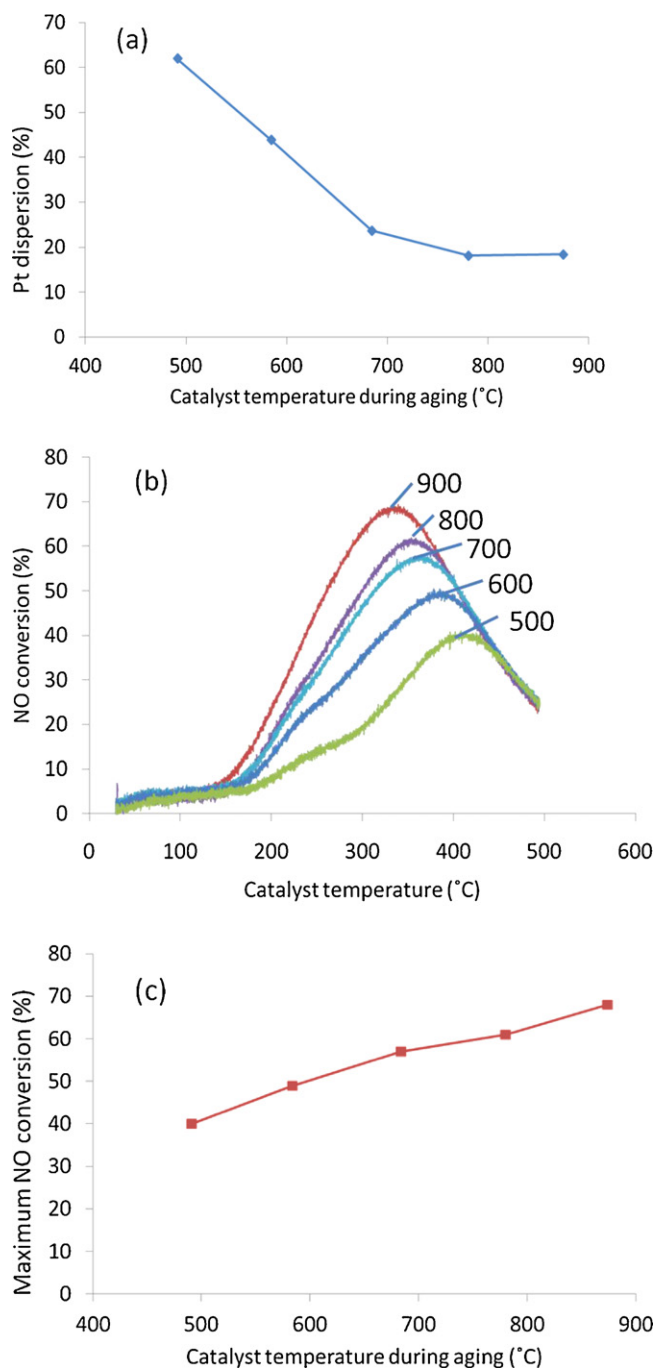


Fig. 2. (a) Platinum dispersion, (b) NO conversion and (c) maximum NO conversion versus aging temperature for the degreened catalyst and subsequent aged in Ar for 2 h (600, 700, 800 and 900 °C).

different dispersion, the two samples show similar NO oxidation activity.

3.4. Effect of O_2

Oxygen has been found to provoke platinum redispersion at low temperature, i.e. below 600 °C, and to cause or accelerate the sintering at higher temperatures [12,13,21]. The effect of oxygen treatment is compared with aging in Ar is shown in Fig. 4. The sintering rate seems to be similar up to aging at 700 °C since the dispersion curves in Fig. 4 are parallel up to this temperature. At 800 °C, the sintering of M- O_2 continued, while the dispersion

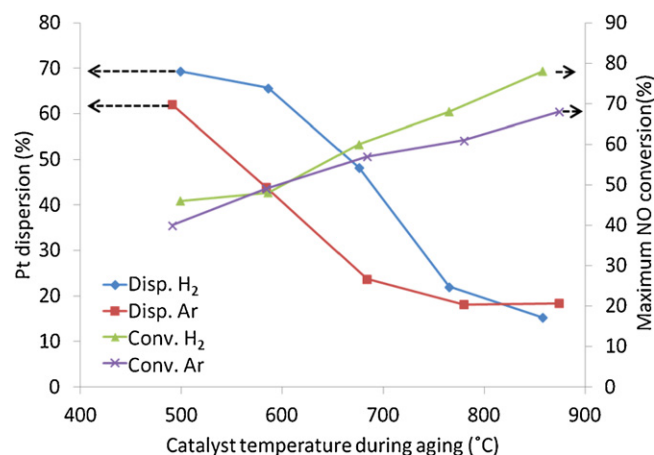


Fig. 3. Platinum dispersion and maximum NO conversion versus aging temperature for the sample aged in 1% H_2 and comparison with the sample aged in Ar. At 500 °C the samples were degreened only.

started to level out for M-Ar. In addition, the catalyst aged in O_2 atmosphere reaches a significantly lower platinum dispersion, 7% versus 18%. It can be concluded that in O_2 atmosphere the sintering was extended compared to the case where the aging was conducted in inert gas. Although the evolution of the dispersion of M- O_2 presents many similarities with M-Ar, the NO oxidation activity profile has little in common. Indeed, despite a moderate loss of dispersion after the first aging at 600 °C in O_2 , its maximum NO oxidation activity increased tremendously from 48% to 71%. For comparison, M-Ar exhibited a similar conversion (68%) after full aging at 900 °C and with a dispersion of 18%. Moreover the performance of M- O_2 reached an optimum after the 700 °C aging before decaying after subsequent aging. Oxygen treatment not only favored the sintering, but the trends for the maximum NO oxidation was also very different from the sample aged in Ar only.

3.5. Effect of sulfur compounds

We have investigated the influence of SO_2 during aging of Pt/ Al_2O_3 . In more detail, we aged one sample in 30 ppm SO_2 and another in 30 ppm SO_2 + 10% O_2 . The presence of oxygen influences the storage of sulfur by the nature and the amount of formed species [22,23]. The dispersion and activity for the sample aged in SO_2 , denoted M- SO_2 , are shown in Fig. 5. After the first aging at 600 °C,

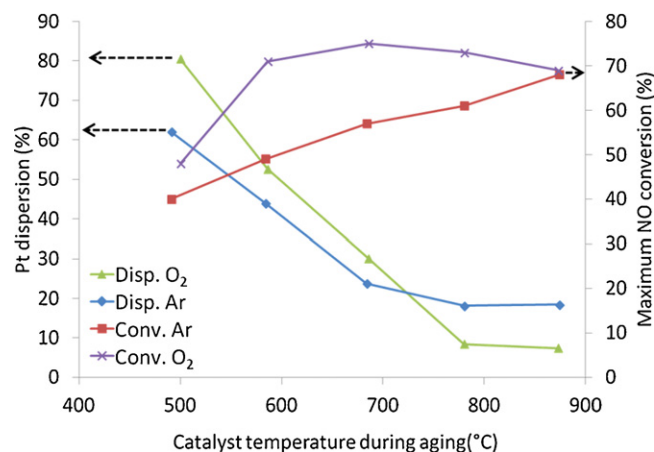


Fig. 4. Platinum dispersion and maximum NO conversion versus aging temperature for the sample aged in 10% O_2 and comparison with the sample aged in Ar. At 500 °C the samples were degreened only.

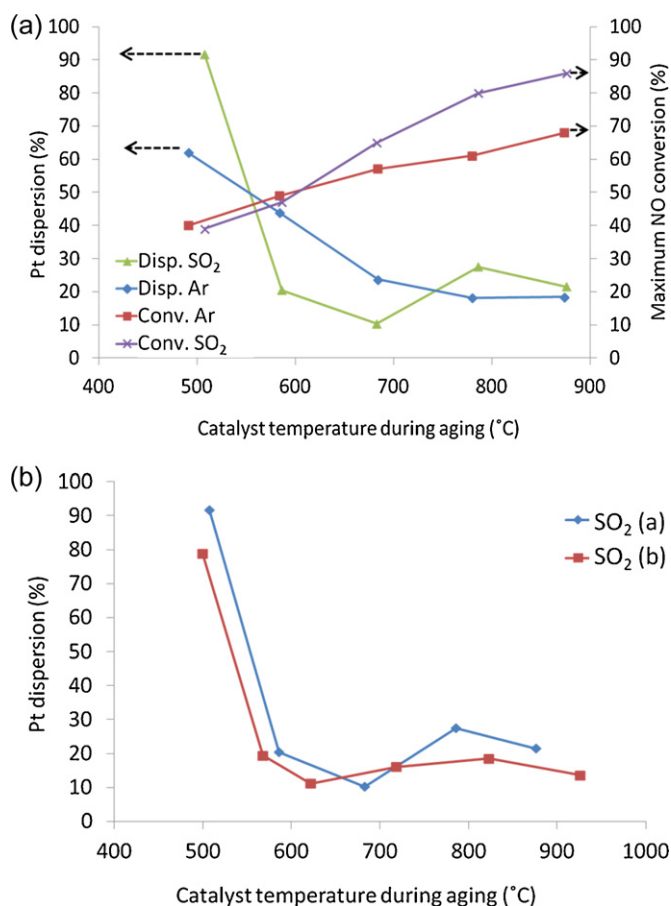


Fig. 5. (a) Platinum dispersion and NO conversion for the sample aged in 30 ppm SO₂ and comparison with the sample aged in Ar. (b) Evolution of Pt dispersion for two samples aged in 30 ppm SO₂. At 500 °C the samples were degreened only.

the dispersion of M-SO₂ decreased significantly and was already at 20%, which is comparable to the dispersion of M-Ar after the last aging step at 900 °C. Surprisingly, the similar dispersion for these samples did not result in the same NO oxidation activity. The maximum NO conversion was 68% for M-Ar with dispersion of 18% and only 47% for M-SO₂ with dispersion of 20%. The activity was instead similar for the M-Ar and M-SO₂ samples aged at the same temperature (600 °C), even though the dispersion was very different. Further, the dispersion curve of M-SO₂ presents an interesting feature: the CO uptake increased after aging at 800 °C yielding a higher dispersion (Fig. 5a). Redispersion of Pt particles has been observed at lower temperatures [13,24,25]. The dispersion increase was reproduced on a second sample aged in SO₂ with the same conditions as M-SO₂. The results for these two catalysts are shown in Fig. 5b. It should be mentioned that during the repeated experiment in Fig. 5b the thermocouples were placed differently, causing differences in the intra-catalyst temperature during aging. The increase in CO chemisorption can also be explained by the presence of stable residues of sulfur on the platinum surface after lower aging temperatures that do not desorb during the reduction treatment with 2% H₂ at 400 °C and affect the dispersion measurements. After subsequent aging treatments, M-SO₂ showed higher maximum conversion than M-Ar. Aging in SO₂ yielded a lower operating temperature and a higher optimum conversion.

The addition of oxygen in sulfur-containing aging atmosphere at 600 °C resulted in a dispersion loss similar to M-SO₂ (Fig. 6). Once again, as seen for M-SO₂, SO₂ has a significant impact on sintering at relatively low temperature since O₂ is not expected to induce a large decrease in dispersion as seen in Fig. 4. However, the ability

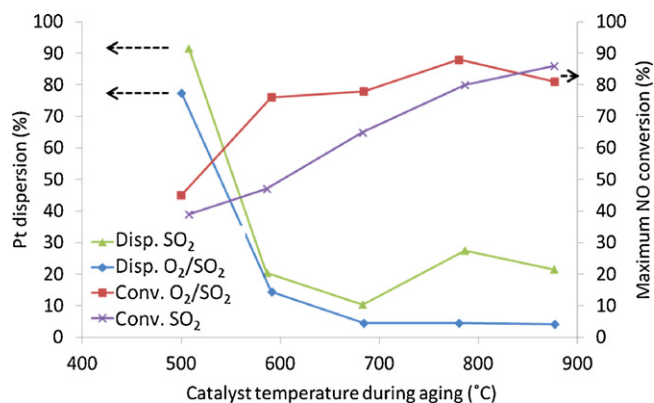


Fig. 6. Platinum dispersion and maximum NO conversion versus aging temperature for the sample aged in 30 ppm SO₂ + 10% O₂ and comparison with the sample aged in SO₂ alone. At 500 °C the samples were degreened only.

of oxygen to reach very low dispersion at high aging temperature is verified for M-SO₂/O₂. The apparent redispersion feature observed on M-SO₂ is absent on M-SO₂/O₂. Thus, the trends for the dispersion for the M-SO₂/O₂ are similar to M-SO₂ at low aging temperatures and M-O₂ at high aging temperatures. Similarly to the M-O₂ sample the M-SO₂/O₂ results in a significant increase of NO oxidation activity already after aging at 600 °C, which was not observed for M-SO₂. In addition, the activity dropped slightly after the 900 °C aging for the M-SO₂/O₂ sample, which was also observed for M-O₂. The combination of 30 ppm SO₂ and 10% O₂ as aging atmosphere gave the best conversion among all the samples (88% after aging at 800 °C, see Fig. 6). After the aging at 900 °C in SO₂ + O₂ the sample was characterized using TEM. The resulting STEM images are shown in Fig. 7. Many large particles are observed and in the image on the right, with higher magnification, the facets of the particles can be clearly seen.

Another experiment was conducted in order to further investigate the influence of SO₂ on the dispersion and activity of Pt/Al₂O₃. In this experiment, a long-term aging in reaction conditions (500 ppm NO and 8% O₂) including 30 ppm SO₂ was performed. Since the dispersion of M-SO₂ and M-SO₂/O₂ significantly decreased at only 600 °C, this experiment was conducted at a temperature as low as 250 °C on an extra sample after degreening at 500 °C and reduction at 450 °C in 2% H₂ (30 min). The dispersion and activity were measured, as described in Section 2, before and after the long-term aging. Before the dispersion measurement the catalyst was pretreated with hydrogen at higher temperature (450 °C) compared to the other samples in order to remove the sulfur species from platinum and to reduce platinum. This increase in reduction temperature is justified by the large sulfate loading expected after the 22-h exposure in conditions favorable to sulfate formation. Additionally, the conversion of NO along the 22-h experiment was measured but only minor changes were observed during the SO₂ exposure. The results from the CO chemisorption show that sintering occurred to a large extent. The dispersion decreased from 65% for the fresh case to 25% for the aged case. The decrease in dispersion was confirmed by STEM experiments, see Fig. 8. Several larger particles are visible, but also many particles remain small. Thus the SO₂ + O₂ induced sintering at low temperature results in particles with a broad range of particle sizes. The NO oxidation activity test revealed that the maximum conversion increased to 76% after this aging (Fig. 9). This value is comparable to the conversion reported for M-SO₂/O₂ after the first two aging temperatures (600 °C and 700 °C). However, the dispersion was lower for the latter cases (Fig. 10). Thus, the SO₂ + O₂ mixture has also other effects than just lowering the dispersion. After the long-term aging step, the monolithic sample was used in order to study the desorption of

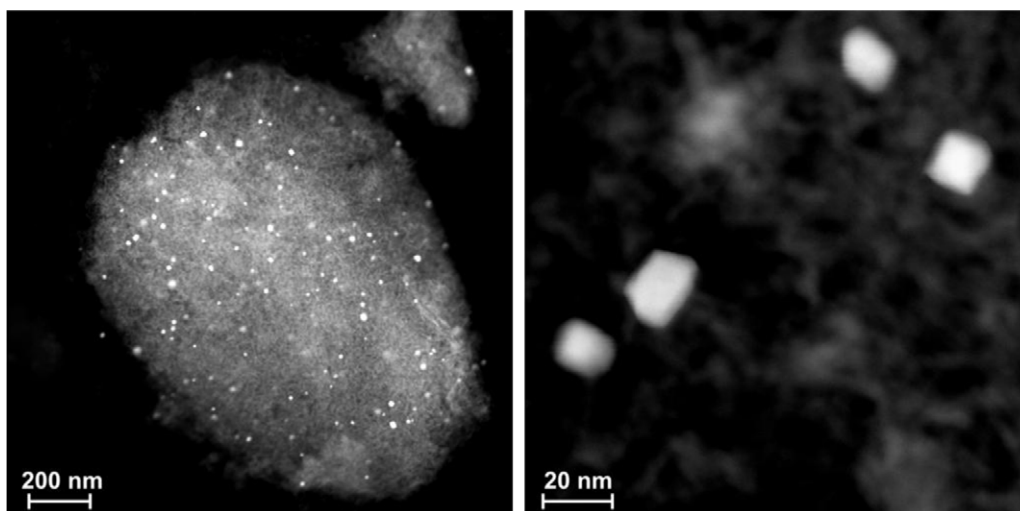


Fig. 7. STEM images of the Pt/Al₂O₃ catalyst aged in presence of 30 ppm SO₂ and 10% O₂, after the full aging procedure.

S-compounds in reducing conditions (2% H₂). After a temperature ramping in Ar up to 800 °C, 2% H₂ was flowed through the sample for 15 min. This step was followed by a rapid cooling of the sample to room temperature in order to limit the platinum coalescence. The dispersion was subsequently measured and a slight but significant increase, from 21% to 25%, was observed. 25% was then taken as the dispersion.

4. Discussion

4.1. Platinum sintering

High temperature and chemically active atmosphere provoke the sintering of platinum particles. Sintering has been explained by the mobility of Pt crystallites, which eventually merged to form larger particles. This mobility is reinforced by higher temperature and formation of new platinum phases or complexes during the aging [15,16]. The presence of oxidative species in the ambient facilitates the latter feature [13,25]. It is obvious that the temperature is an important factor in the sintering process, so rather short aging steps (2 h) were carried out in order to emphasize the contribution of atmosphere on the sintering rate. Further, the sintering rate of platinum has been found to be initially high and decrease with time [12,26].

The results presented here show the effect of different gases on the sintering rate. The synthesis method used leads to well-dispersed catalysts indicated by the high dispersion values obtained for the fresh samples (Table 1). This was also confirmed by STEM measurements (Fig. 1). The samples aged in Ar and O₂, respectively, exhibit similar linear decrease in dispersion for lower aging temperatures. However, the aging is more severe in oxygen-containing atmosphere at higher temperatures. For both samples the dispersion levels off at high aging temperatures, but at a lower value for the sample aged in O₂. However, aging in H₂ limits the particle migration since platinum remains in metallic state in reducing condition. In an oxygen atmosphere, sintering rate has been found higher than in H₂ at temperature above 600 °C. The model mechanism established by Fiedorow et al. [27] suggests the migration of molecular species such as PtO that have higher mobility on the support and require a lesser energy to escape a particle. At 600 °C, sintering in H₂ is only minor but the sintering rate is increased with temperature (Fig. 3).

The presence of SO₂, alone or combined with O₂, accelerates the sintering and already after the aging at 600 °C the dispersion is close to the minimum level. The STEM analysis of M-SO₂/O₂ after

the complete aging procedure disclosed the presence of large metal particles evenly spread on the support, as presented in Fig. 7. The unexpected increase of dispersion after aging at 800 °C for M-SO₂ has been repeated on another sample subjected to the same treatment as M-SO₂ (Fig. 5b). The hypothesis of re-dispersion by SO₂ treatment at 800 °C was investigated. The treatment of fully aged M-Ar and M-O₂ in 30 ppm SO₂ at 800 °C did not cause any change in Pt dispersion or NO conversion. Thus we cannot use this condition in order to re-disperse other severely aged samples. It is therefore not likely that there is a real redispersion in our experiments. Another possibility is that some residual sulfur species covering partially the platinum remained on the catalyst even after the hydrogen treatment prior to CO chemisorption. Indeed, the temperature during reduction was only 400 °C, and there might be sulfur remaining on platinum. In addition, it is likely some sulfur compounds present on the alumina support after this treatment, which might spill-over to the platinum. If SO₂ species covering Pt were immobile and kept blocking the same fraction of active sites during the activity test, then the dispersion measured, defined as the fraction of available sites for the reaction, is true but cannot be correlated to the average particle size. Pazmiño et al. [29] have showed using EXAFS that pre-adsorbed sulfur on Pt was displaced from Pt in reaction condition. The same observation was made by Giles et al. on Fe-MFI catalyst [30]. The formation of sulfur species depends on many factors such as the temperature, the presence of water, the partial pressure of SO₂ and O₂ [22,23,28]. SO₂ storage on alumina and Pt/alumina becomes less when exposure temperature increases [23], whereas the stability of sulfates increases with their formation temperature [28]. We therefore expect the formation of stable sulfate in small amount during the SO₂ treatments at 600 and 700 °C. We suggest that the dispersion was slightly underestimated after the first two agings, due to sulfur blocking of the noble metal sites. These compounds were then thermally decomposed during the aging step at 800 °C explaining the following increase of CO chemisorption.

After the dispersion and activity measurements on the long term aged sample with SO₂ + O₂ at 250 °C, a short reduction step at 800 °C with 2% H₂ was performed in order to remove all sulfate adsorbates possibly remaining on the surface. Indeed, a fraction of free surface platinum was recovered, increasing the measured dispersion from 21% to 25%. Although additional sintering may have occurred during the 15-min exposure at 800 °C, this result showed that a small, but significant, fraction of platinum was still covered by sulfur compounds after the long sulfation and the reduction treatment at 450 °C preceding the dispersion measurement. Thus, these results

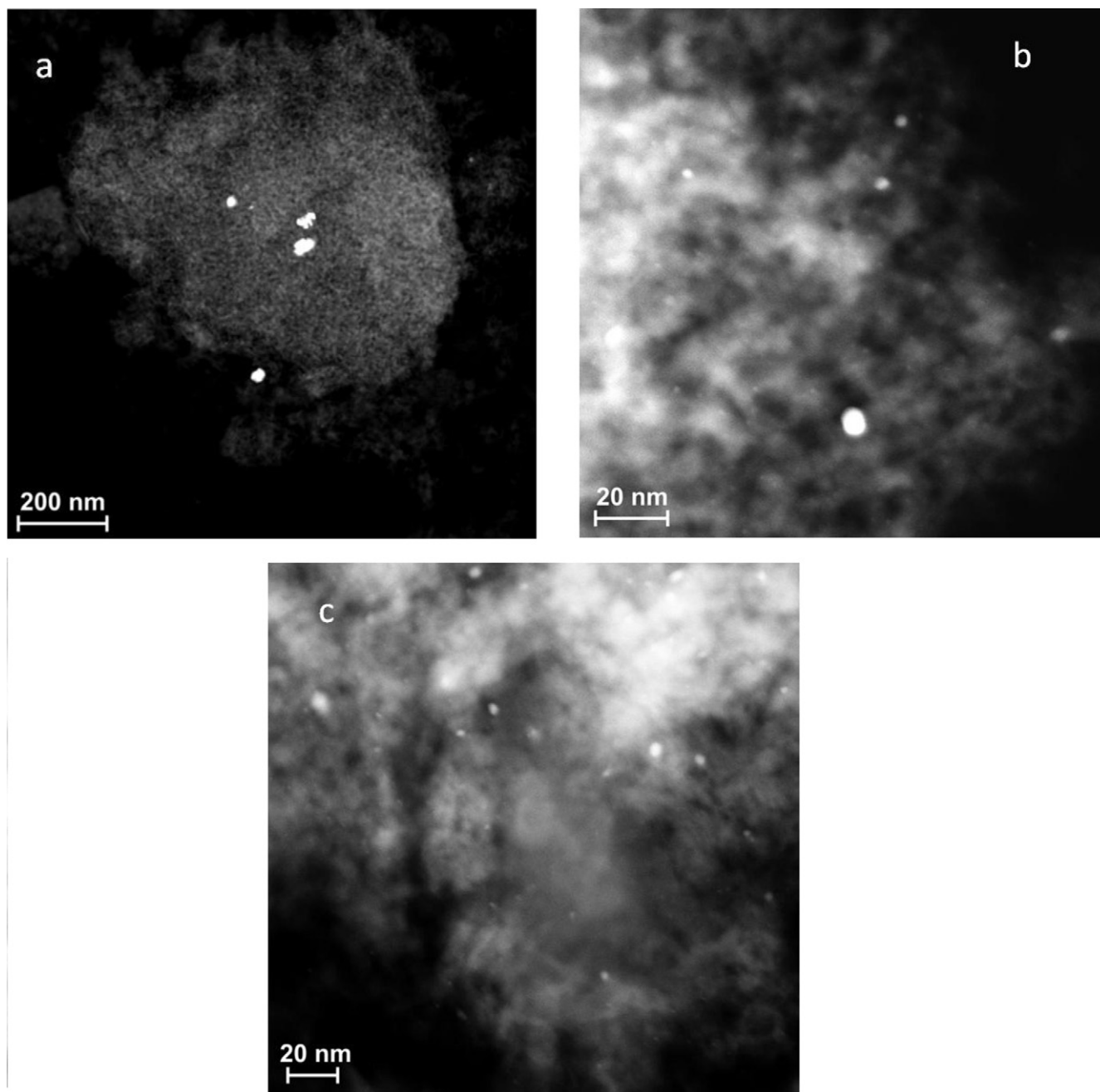


Fig. 8. STEM images of the Pt/Al₂O₃ catalyst aged in presence of 30 ppm SO₂, 8% O₂ and 500 ppm NO for 22 h at 250 °C.

also support that removal of sulfur species can be the reason for the increase in CO chemisorption occurring at 800 °C. Since the apparent loss of dispersion due to the coverage of platinum by sulfur was small, the dispersion drop observed after short SO₂ exposure at 600 °C for M-SO₂ and M-SO₂/O₂ samples can to a large extent be attributed to true sintering promoted by the presence of SO₂. Unlike M-SO₂, M-SO₂/O₂ demonstrated a monotonic loss of dispersion even though O₂ promotes the storage of SO₂ on Pt/Al₂O₃ [23].

The long-term aging at 250 °C in NO+SO₂+O₂ in this work enabled to decrease drastically the dispersion to 25% which is remarkable at such low temperature. The particle size was studied with STEM and some resulting images with different resolution are presented in Fig. 8. The agglomeration of platinum particles was confirmed by the presence of large particles (Fig. 8a). Fig. 8b and c show that small particles, similar to the ones observed on the fresh

catalyst, still remained after the low temperature treatment. Particles with intermediate size, between 5 and 10 nm, are also present and visible on these images. This value is comparable with the dispersion after full aging of M-Ar, M-SO₂ and M-H₂. After the long term NO+O₂+SO₂ experiment and the subsequent regeneration with hydrogen at 800 °C, the measured dispersion was 25%, which is similar to the dispersion of M-SO₂ after exposure at 600 °C.

4.2. NO oxidation

The oxidation of NO is known to be structure sensitive, i.e. the activity depends strongly on the particle size [4,8,9]. Our aging study shows that some factors other than the size of the particles play a role in the performance of the catalyst. The performance of M-Ar got noticeably better after the last aging (Fig. 2a) while the dispersion stayed stable at 18%. The opposite feature was noted

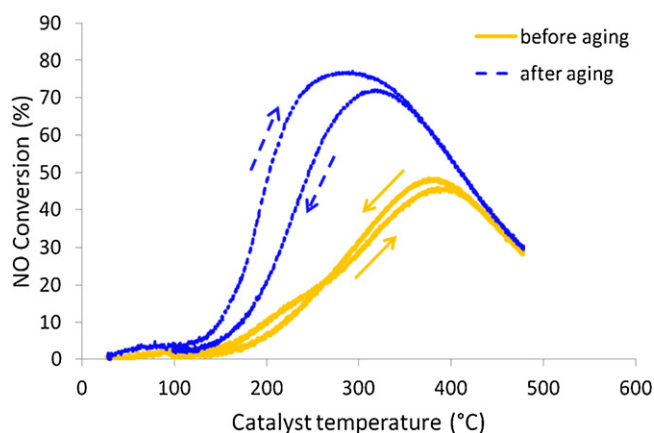


Fig. 9. NO conversion to NO_2 during NO oxidation experiment (500 ppm NO, 8% O_2 , 3 L/min) conducted before and after long term aging: 22 h at 250 °C in 500 ppm NO + 8% O_2 + 30 ppm SO_2 . After aging, the catalyst was regenerated with 2% H_2 (40 min at 450 °C). Also shown is the hysteresis during heating (5 °C/min) and subsequent cooling (−5 °C/min).

on M-O_2 , which presented a decrease in activity in parallel of a dispersion loss (Fig. 4) at high aging temperatures. This deactivation was also observed for $\text{M-SO}_2/\text{O}_2$ after the final aging at 900 °C (Fig. 6). This effect might be attributed to that samples aged at 900 °C in oxygen containing environment facilitates the formation of stable platinum oxides during the subsequent NO oxidation experiment. Platinum oxide is less active for NO oxidation than metallic platinum [6,8]. M-O_2 clearly shows that larger platinum particles do not always exhibit the best NO oxidation activity. The

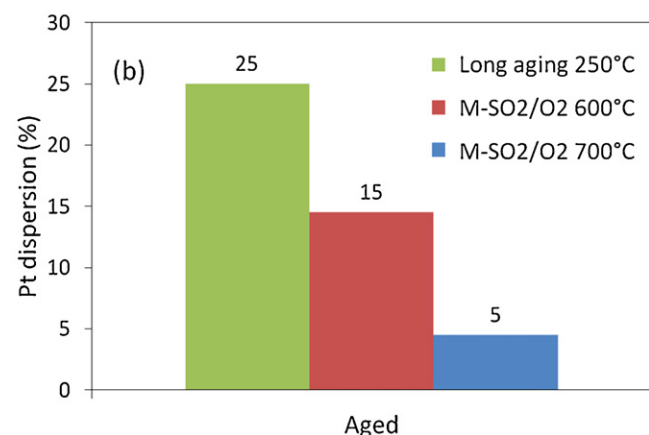
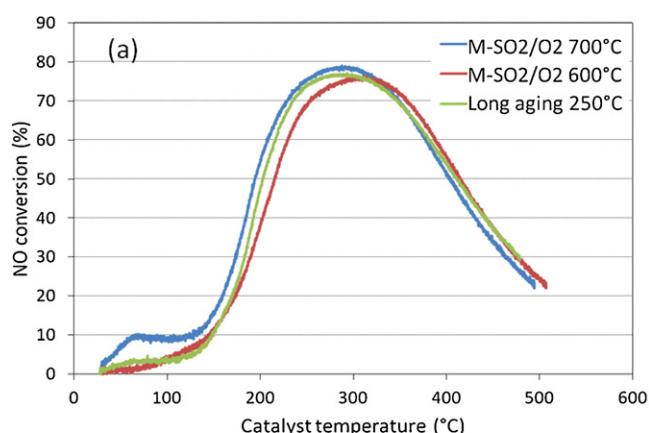


Fig. 10. (a) Activity profiles and (b) dispersion of $\text{M-SO}_2/\text{O}_2$ aged at 600 °C, $\text{M-SO}_2/\text{O}_2$ aged at 700 °C and the long-term aged catalyst after aging.

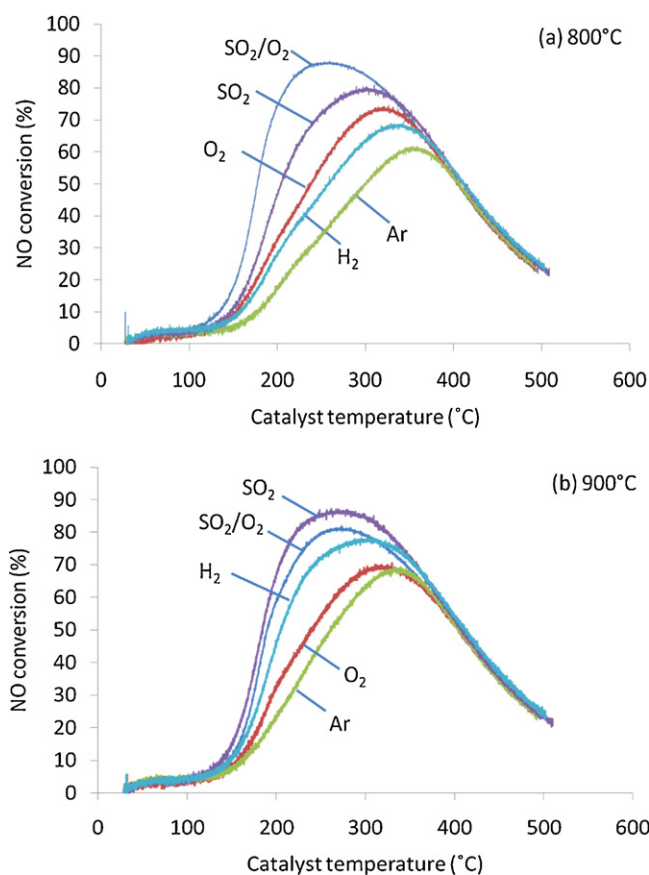


Fig. 11. Comparison of the NO conversion profiles during NO oxidation experiments for all the samples after aging at (a) 800 °C and (b) 900 °C.

effect of O_2 on sintering up to 700 °C, is similar to the sample aged in Ar, but O_2 has a unique influence on the NO oxidation conversion. A dramatic increase of the conversion after the first aging at 600 °C was reported for M-O_2 and $\text{M-SO}_2/\text{O}_2$ (Figs. 4 and 6). We suggest that one possible reason might be the enhanced ability of the particles to dissociate O_2 and bind atomic oxygen after aging in oxygen containing environment. It has been found that certain oxygen coverage was necessary to activate the NO oxidation on Pt [31,32] and that the rate limiting step for NO oxidation is oxygen adsorption. On the other hand, formation of stable platinum oxide layer inhibits NO oxidation [8,33]. Therefore the conversion is likely better on particles that can easily dissociate and adsorb oxygen (chemisorbed oxygen and not platinum oxides). Further, Fig. 7b shows that faceted particles were formed during aging with SO_2 and O_2 . This morphology is characterized by a high fraction of plane sites and also edge and corner sites. The flat facets are more resistant to oxide formation due to their high degree of coordination while steps are efficient in O_2 dissociation [34], which is necessary for forming chemisorbed oxygen. The morphology evolution of platinum particles, between fresh and aged catalyst, could be one reason for the activity differences.

Fig. 11 shows the conversion profiles of all the samples after aging at 800 °C (a) and 900 °C (b). The samples can be gathered in two groups, based on the dispersion. One group is the samples that were aged in the presence of O_2 (M-O_2 and $\text{M-SO}_2/\text{O}_2$) and the other group is in absence of O_2 (M-Ar , M-H_2 , M-SO_2). The first group had dispersions of about 4–8% for 800 °C aging and 4–7% for 900 °C aging. However, the NO oxidation activity does not follow the same trend as the dispersion. For the second group the corresponding results were 17–25% and 17–20%, respectively. The best overall performance is attributed to $\text{M-SO}_2/\text{O}_2$ aged at 800 °C, 88% between 245

and 260 °C (Fig. 11a). The M-O₂ sample aged at 800 °C had a similar dispersion as the M-SO₂/O₂ sample after the same aging temperature. However, M-SO₂ still exhibited a higher NO oxidation activity than M-O₂ even though the dispersion was 28% for this sample compared to 8% for M-O₂. Thus it is clear that SO₂ has a promoting effect on the NO oxidation, which is not only related to the decrease in dispersion. After the 900 °C aging the samples with SO₂ present during the aging still showed the highest activity, but now M-SO₂ was the best. Both M-SO₂/O₂ and M-O₂ had a decrease in activity after this aging, likely due to formation of stable platinum oxides. However, the other samples became more active after 900 °C aging, in particular M-H₂ performance was greatly improved after the last aging.

One reason for the beneficial effect of sulfur present during aging could be that sulfated samples are more acidic. Yoshida et al. [35] measured the acid strength (pK_a) for ZrO₂ and sulfated ZrO₂ and observed a large decrease from 9.3 to –13.2. They also found that platinum on more acidic supports exhibited a larger fraction of metallic platinum [36]. We have also observed previously that larger amounts of platinum oxides are formed on barium/alumina support compared to alumina only [37]. The reason for this is that barium is more alkaline. An acidic support is electrophilic, which results in that platinum donates electron density from 5d band to the support. Platinum has therefore less electron density to donate to oxygen, which is required for the formation of platinum oxides. Thus, an acidic support suppresses platinum oxide formation. Since platinum oxides are less active for NO oxidation than metallic platinum [6,8] one reason to that the sulfated platinum alumina samples exhibits so high activity could be that the support acidity is enhanced by stable sulfate species

The NO conversion curve showed hysteresis loop when ramping the temperature up or down, which is illustrated in Fig. 9. The results both before and after the long-term aging are presented. For the degreened catalyst the conversion was quite similar for the up and down temperature ramp, it was even slightly better for the cooling. However, the trend was changed after aging and the conversion, became much lower during the cooling phase. The activity loss between the two legs decreased both the maximum conversion and the temperature window for NO conversion. Also for the other samples the hysteresis behavior was investigated, but unfortunately the cooling rate was not controlled in these experiments. M-SO₂/O₂ and M-O₂ have the same behavior as the long term NO + O₂ + SO₂ aged sample, with a more intense hysteresis for the aged sample. At the end of the aging process, M-H₂, M-Ar and M-SO₂ show a better or equivalent maximum of conversion during the cooling, but simultaneously a lower activity at low temperature. The inverse hysteresis phenomenon was studied by Hauptmann et al. [20] and was ascribed to the reversible oxidation of platinum by NO₂ produced during the experiment.

Our results indicate that the hysteresis is increased when the aging is conducted in atmosphere containing oxygen. We suggest that aging in oxygen at high temperature facilitates the formation of platinum oxides during the subsequent NO oxidation at lower temperatures. However, the aged catalysts containing large particles are usually suggested to be more resistant to Pt oxidation than fresh and high-dispersion catalysts. Yet a hysteresis, with higher conversion during the cooling, was found for fresh catalyst and an inverse hysteresis for low-dispersion M-SO₂/O₂ and M-O₂ was observed. There are several possible explanations for this behavior, one being that the particles present on the latter catalysts might be readily oxidized to form platinum oxides, due to the aging procedure. The hysteresis observed on the fresh catalysts can alternatively be due to that the fresh catalyst is less active. This results in less amount of NO₂ produced and this might lead to less oxidation of platinum. The NO coverage might also be a reason of hysteresis since the catalyst is saturated at room temperature with NO before the ramp.

As the temperature increases, NO desorbs and is converted. As NO desorbs, O₂ can dissociate and adsorb on the surface, which is an important step for the NO oxidation. However, results from kinetic modeling show that the NO coverage is quite low already at 250 °C [37], therefore this explanation is not likely for medium and high temperatures.

The activity measured on the catalyst after the long term aging at 250 °C in SO₂ was compared with the activity profiles obtained after aging at 600 and 700 °C for M-SO₂/O₂ in Fig. 10 (a). The production of NO₂ for the long term aged sample at low temperature with SO₂ and O₂ was between the NO oxidation activity for M-SO₂/O₂ aged at 600 and 700 °C. These results show that similar activity for NO oxidation could be obtained with very different treatments in term of temperature and duration of exposure. Interestingly, similar performances were obtained with significantly different dispersion as shown in Fig. 10(b). The 22-h treatment with SO₂ resulted in high activity and rather high dispersion. STEM analysis of the Pt particles showed that the long aging created larger particles (Fig. 8) but, on the other hand, left a large fraction of the small initial particles unchanged (Fig. 8). M-SO₂/O₂, after the last aging, presented only large particles (Fig. 7). That difference in particle size distribution between the two SO₂ treatments explains the difference in dispersion. The long treatment has therefore the advantage of increasing the catalytic activity for NO oxidation while limiting the dispersion loss, which is a factor for deactivation for other oxidation reactions.

5. Conclusion

The aging behavior for model diesel oxidation catalysts was examined in this work. More specifically the effect of varying the gas composition during aging of 1 wt.% Pt/Al₂O₃ was investigated. The aging was done stepwise at 600, 700, 800 and 900 °C after degreening at 500 °C. Five samples were aged in this way, but with different gas compositions; Ar, 10% O₂, 1% H₂, 30 ppm SO₂ and 30 ppm SO₂ + 10% O₂. After each aging step the dispersion and NO oxidation activity was detected. Before the dispersion measurement the sample was treated with hydrogen and platinum thereby regenerated. For the sample aged in Ar the dispersion decreased quite linearly up to 700 °C and after that started to level out. The presence of hydrogen made the deactivation rate slower, while for aging in O₂ the trends were similar to aging in Ar. However, after aging in O₂ a significantly lower dispersion were obtained at higher temperatures. After aging in SO₂ and SO₂/O₂ the dispersion decreased dramatically already for the 600 °C aging. Thus SO₂ induces platinum migration, which has also been observed earlier.

When the platinum dispersion decreased the NO₂ oxidation activity increased, due to that the reaction is structure sensitive. After aging at 600 °C the dispersion for M-Ar was 40% and for M-O₂ 48%. However, the NO oxidation activity was significantly higher for the sample aged in oxygen, even though the dispersion was only slightly higher. For this case, after aging at 600 °C, the maximum NO conversion was 49% for M-Ar and 71% for M-O₂. To conclude it is not only the platinum particle size that influences the NO oxidation activity, but also the environment used in the aging. Oxygen adsorption is believed to be the rate limiting step for NO oxidation and we observe that when oxygen is present during aging at lower temperatures it is beneficial for the NO oxidation activity.

Further, sulfur has a large beneficial effect on the NO oxidation activity after regeneration of the samples. For example, after aging at 800 °C the SO₂ aged sample showed a maximum NO oxidation of 80%, while M-O₂ converted 73% of the NO to NO₂. However, the dispersion for the M-SO₂ sample was higher, 25% versus 8%. These results clearly show that both the dispersion and the gas atmosphere during aging are important for the NO oxidation activity. The best activity (maximum NO oxidation activity of 88%) was observed

for M-SO₂/O₂ after 800 °C aging. One reason for the beneficial effect of SO₂ might be that sulfated alumina is more acidic than pure alumina. The acidic support could suppress the formation of platinum oxides and thereby increasing the NO oxidation activity.

A 22-h aging at 250 °C in a mixture containing 500 ppm NO, 8% O₂ and 30 ppm SO₂ resulted in a significant decrease of Pt dispersion, from 65% to 25%, which shows the ability of SO₂ + O₂ to promote platinum sintering. This was confirmed by STEM measurements, where large platinum particles were observed. In addition, many small particles remained thus this long term SO₂ + O₂ treatment at 250 °C resulted in a broad distribution of particle sizes. This treatment resulted in an increase of the maximum NO conversion from 45% to 76%. This activity is between the activity for the M-SO₂/O₂ sample aged at 600 and 700 °C. Interestingly, the dispersion after the long term aging was 25%, but only 15 and 5% for the aging at 600 and 700 °C. To conclude the long term aging at 250 °C results in a catalyst with high NO oxidation activity, but still a quite high dispersion.

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